UNIVERSITEIT GENT

FACULTY OF ENGINEERING

In situ X-ray absorption study of the total oxidation of propane over $CuO\text{-}CeO_2/Al_2O_3$

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Laboratory for Chemical Technology

IDECAT Integrated Design of Catalytic Nanomaterials for a Sustainable Production

Overview

- Introduction
- Experimental & analysis procedure
- Results
  - In situ XAS measurements
  - Theoretical calculations
- Conclusions

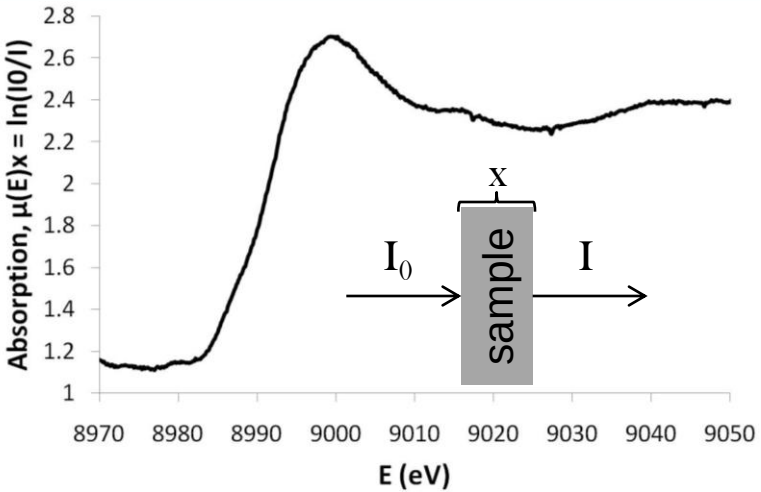
Introduction

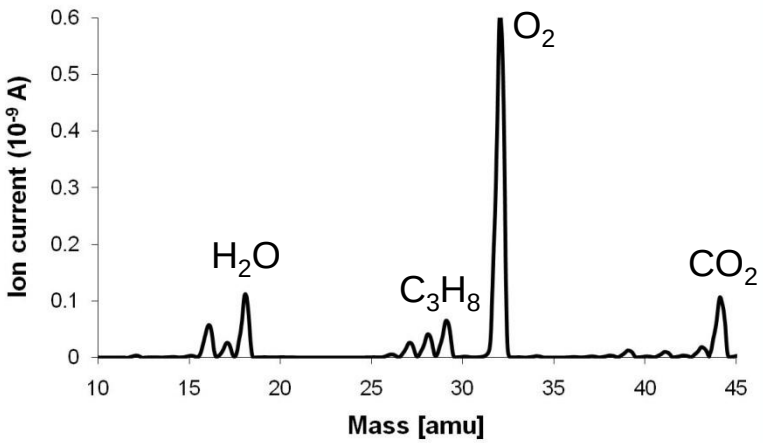
- Objective:

  obtain insight in the structure of the $CuO\text{-}CeO_2/Al_2O_3$ catalyst under working (i.e. red-ox) steady state and transient conditions

- Method:

XANES at Cu K edge •--------• Mass spectroscopy





Introduction

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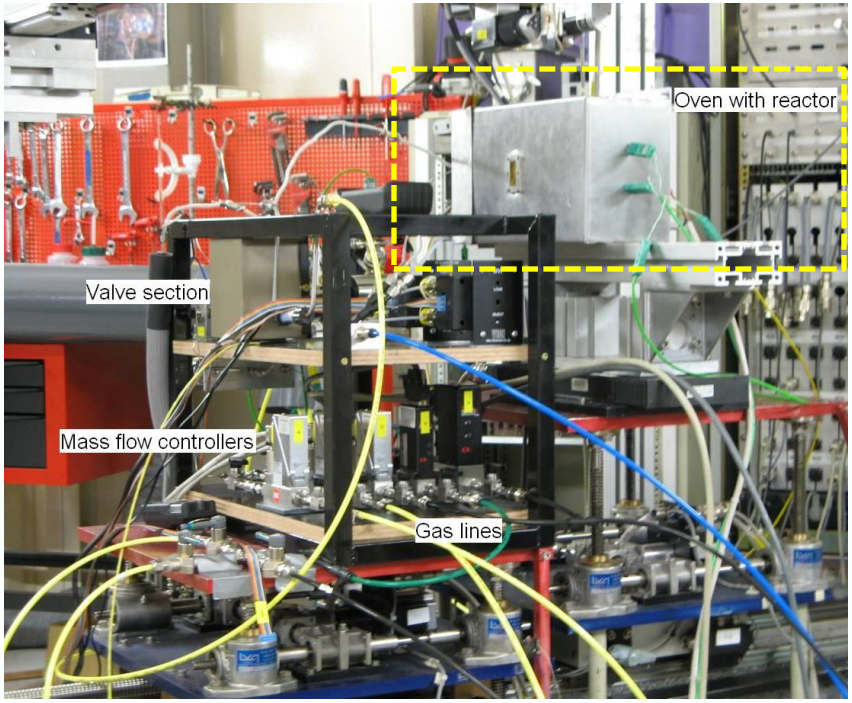
  obtain insight in the structure of the $CuO\text{-}CeO_2/Al_2O_3$ catalyst under working (i.e. red-ox) steady state and transient conditions

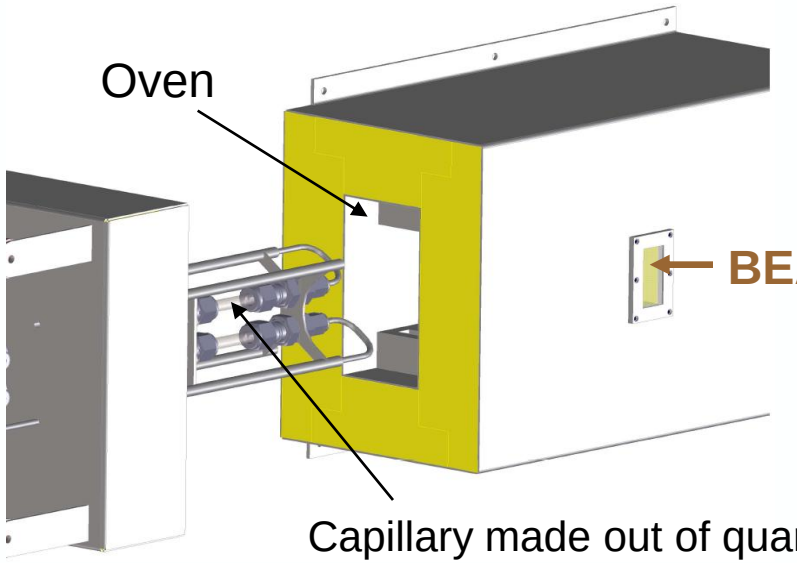
- Method:

XANES at Cu K edge •--------• Mass spectroscopy

Structure of the active phase (e.g. coordination, oxidation state) ⟷ ***Conversion, selectivity***

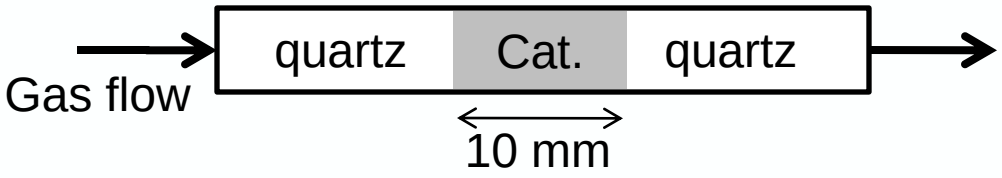
Experimental setup





Capillary made out of quartz
(ID = 0.9 mm, OD = 1.0 mm)

Fixed bed reactor



~5 mg cat. (particle size: 75-100 µm)

Experimental procedure

- Pretreatment:

1. Heating from RT to 423 K under He
2. At 423 K under 10% O_2/He for 1 h
3. Heating under He from 423 K to first reaction temperature

- Step response experiments performed, T= 573-723 K:

1. Catalyst red-ox cycles: He |→ 10%O_2/He → He |→ 2%C_3H_8/He

   Constant flow rate = 1.5 10^{-5} mol/s
2. Total oxidation reaction: He |→ (1%C_3H_8+ 5% or 10%O_2)/He

   Space times = 38.3-127.7 kg s / mol

→ Apart from the transient response, the catalytic system is allowed to reach its steady state in all experiments

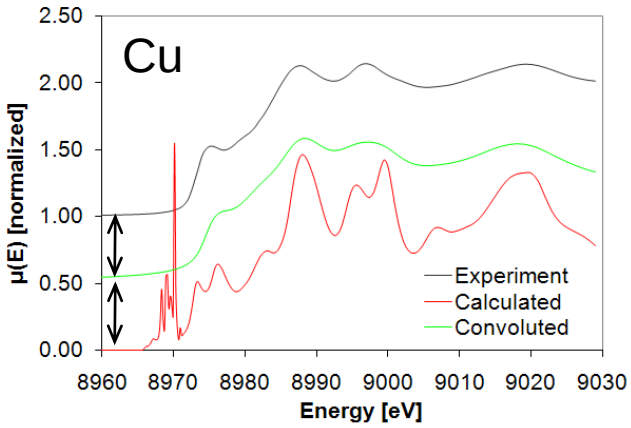
Analysis procedure

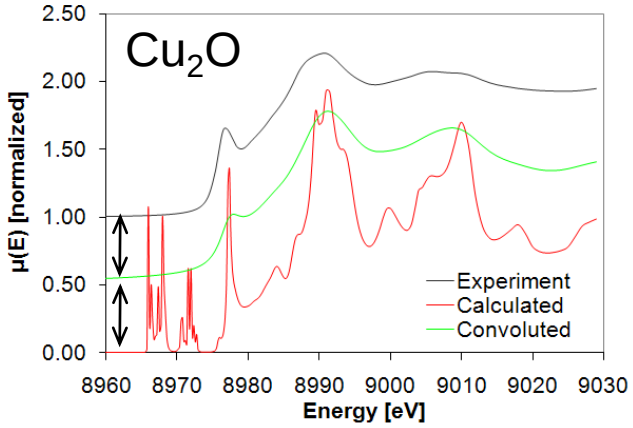
- **MS: 0.1s/amu**
  - amu's followed: 4, 12, 14, 18, 28, 29, 32, 41, 44
  - gas phase compositions: He (internal standard), CO, C_3H_8, O_2, C_3H_6, CO_2

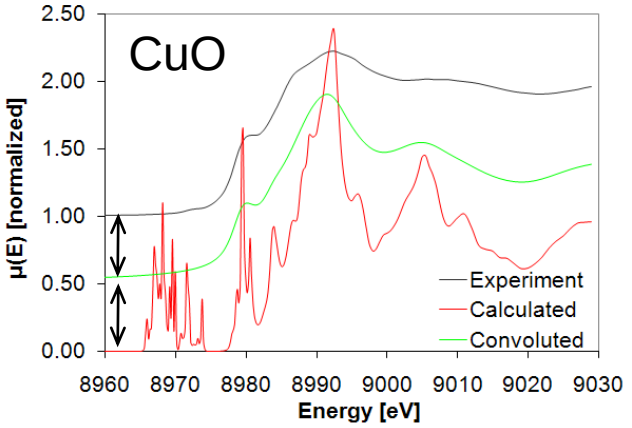
- **XANES: 0.1s/spectrum**
  - Raw data in pixels (of the camera) → **energy calibration** by comparing a Cu foil measured in pixels (taken at ID24) to one measured in eV (taken at the energy scanning beamline BM26)
  - Determination of **edge position**, **background subtraction** & **normalization** of calibrated raw data
  - Solid phase compositions from **spectral de-convolution**:
    - Standard spectra used: oxidized catalyst sample (Cu^{2+}), reduced catalyst sample after treatment with propane (Cu^0), Cu_2O reference sample (Cu^{1+})
    - **Principal component analysis (PCA)** to find number of phases and assess suitability of standards for describing a given set of spectra
    - **Linear combination fitting (LCF)** to quantify the ratio of $Cu^{2+}/Cu^{1+}/Cu^0$

Analysis procedure

- **Theoretical XANES calculations:**
  - FDMNES
  - Muffin-tin approximation
  - Models used: crystal structure of Cu, Cu_2O, CuO
  - Cluster size of 8.3 Å
  - Convolution parameters obtained from the best fit with the references
  - Variance: $$\sigma^2 = 100 \frac{\int \left(\chi_{model}(E) - \chi_{exp}(E)\right)^2 dE}{\int \left(\chi_{exp}(E)\right)^2 dE}$$

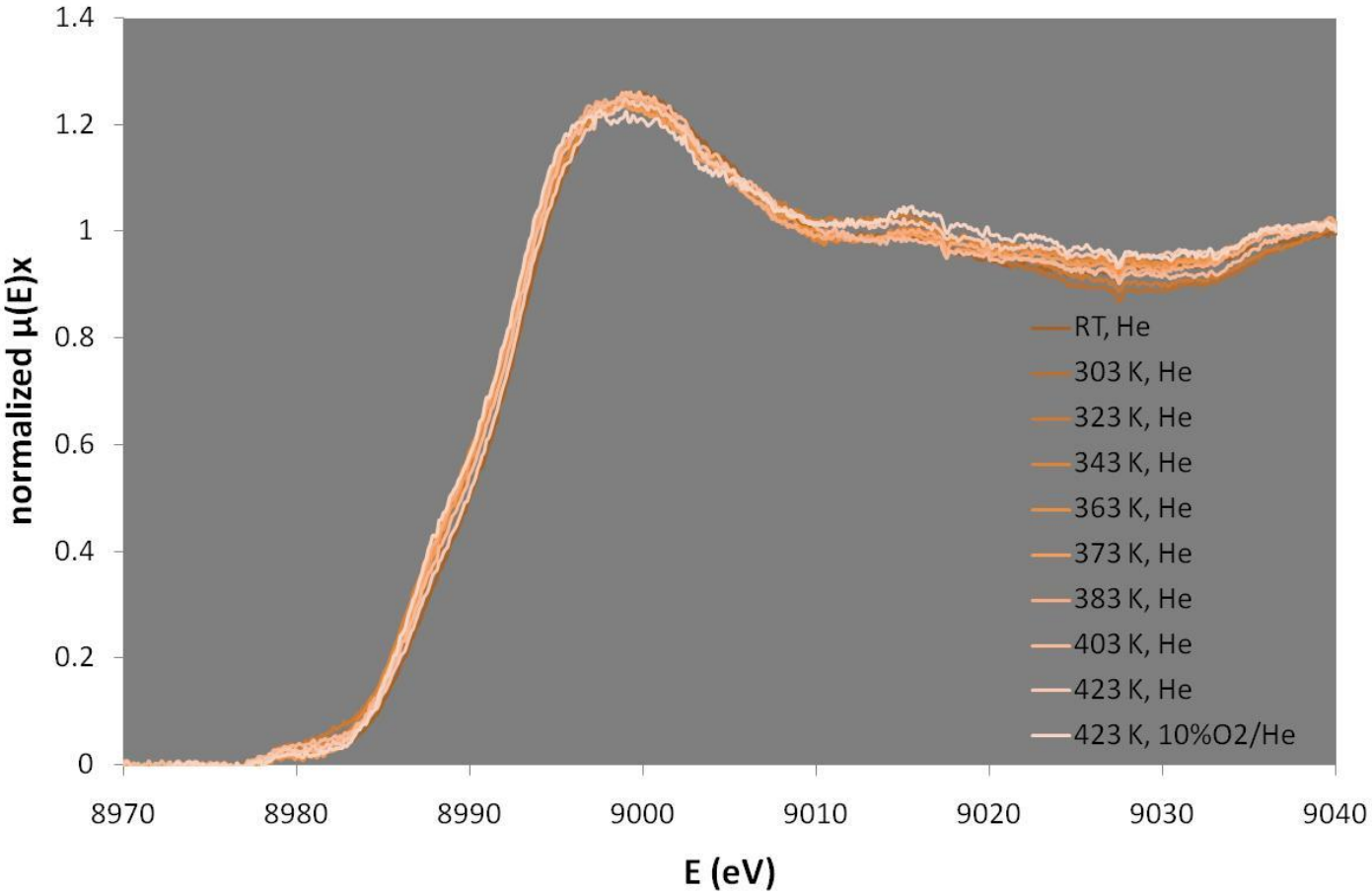






Results - In situ XAS measurements

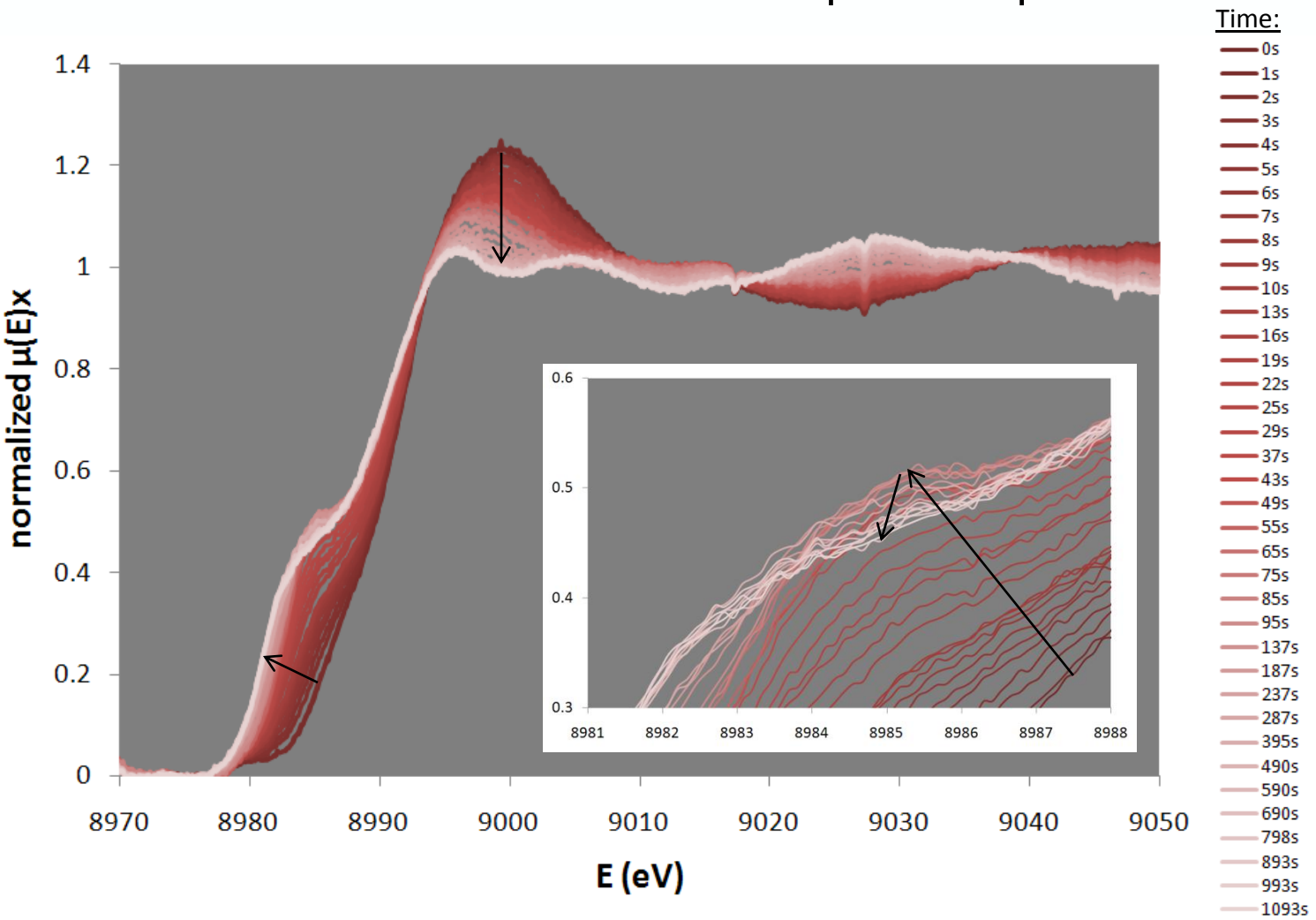
- XANES of the $CuO\text{-}CeO_2/Al_2O_3$: while heating under He and after pretreatment



→ No changes in the spectra

Results - In situ XAS measurements

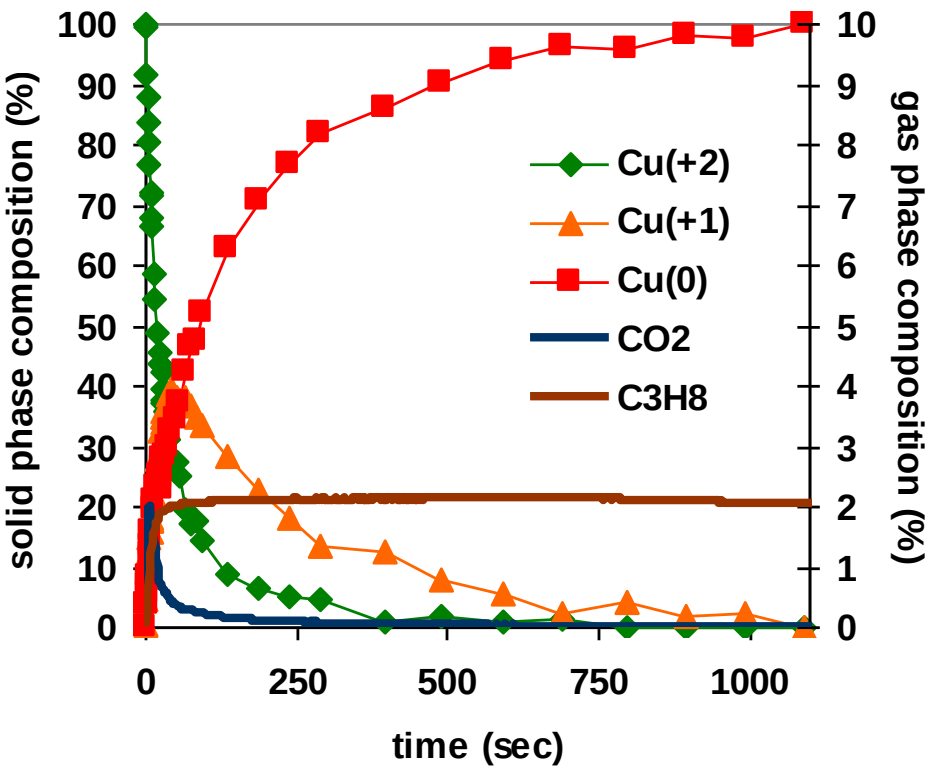
- XANES of the $CuO\text{-}CeO_2/Al_2O_3$: He|→ 2%C_3H_8/He step-response experiment at 723 K



→ Catalyst reduction: a two step process is found

Results - In situ XAS measurements

- Catalyst reduction at 723 K
  1. PCA: 3 components
  2. LCF & MS analysis:



→ Mechanism of catalyst reduction:

Cu^{2+} → Cu^{1+} → Cu^{0}

→ No CO_2 when the catalyst is fully reduced

→ The LCF analysis agrees with the MS results

Results - In situ XAS measurements

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  1. PCA: 3 components
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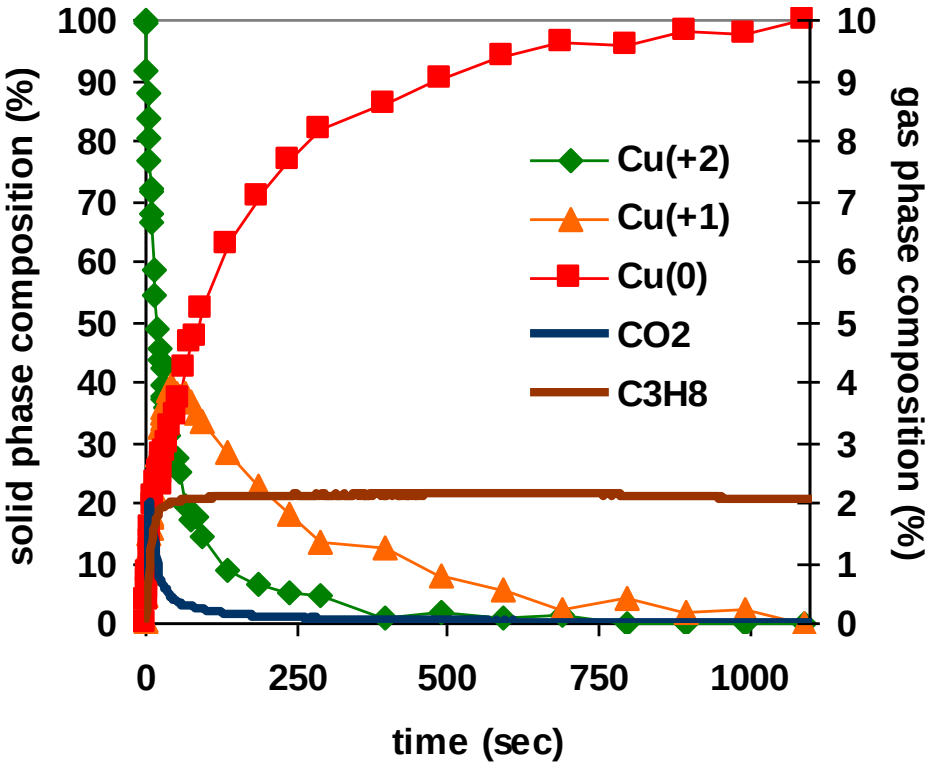

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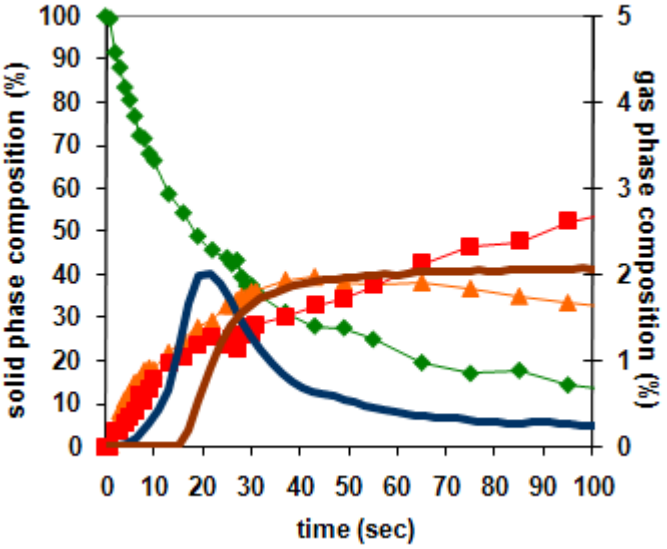
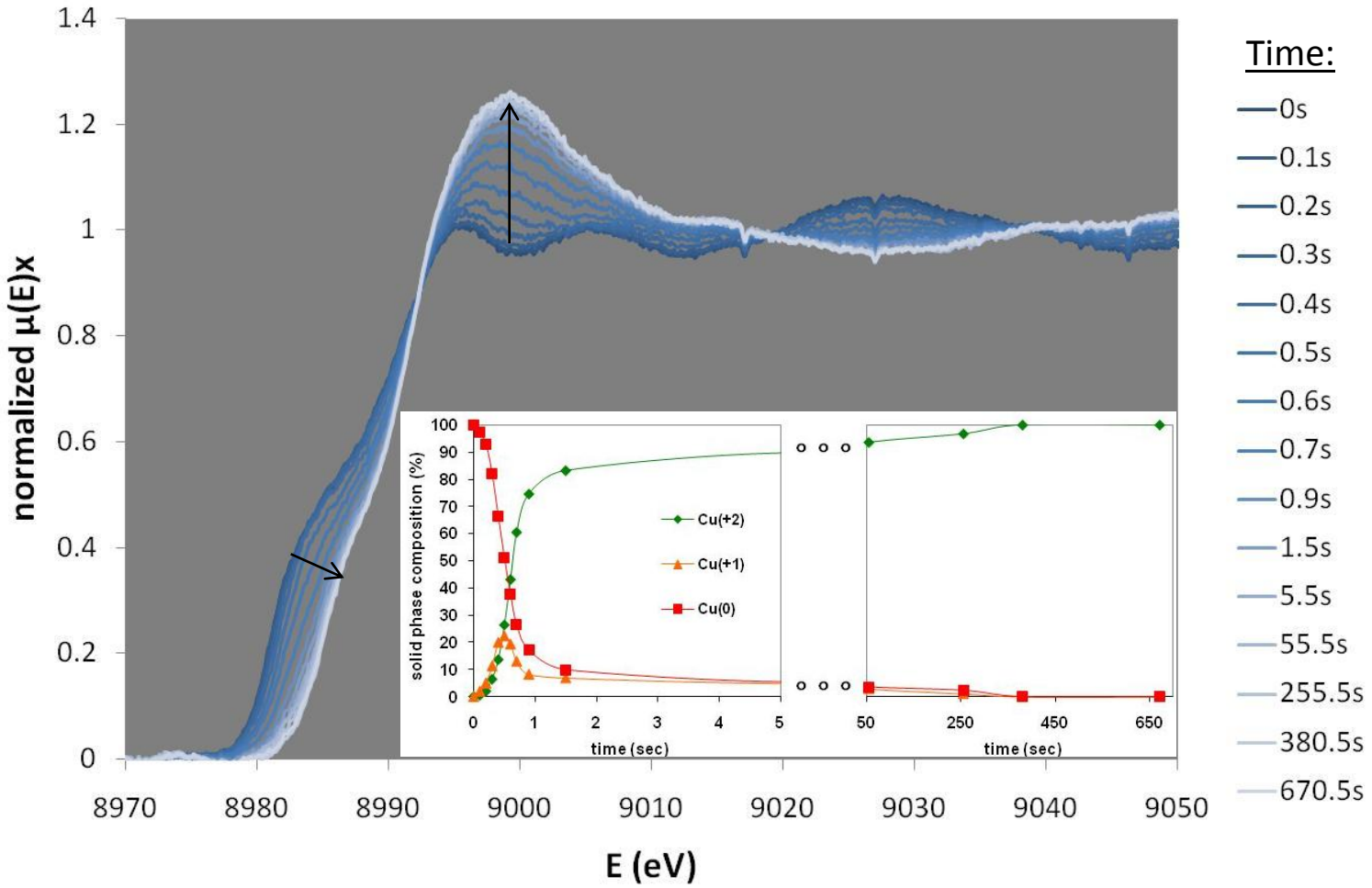


Results - In situ XAS measurements

- XANES of the $CuO\text{-}CeO_2/Al_2O_3$: He|→ $10\%O_2$/He step-response experiment at 723 K

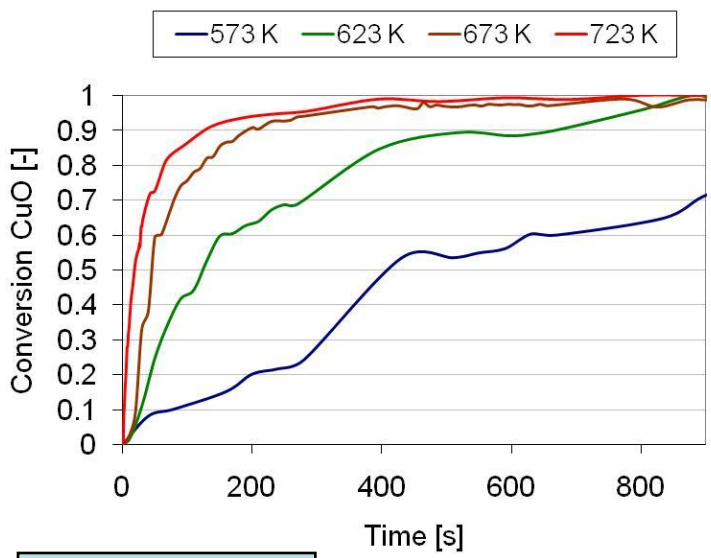


→ Catalyst reduction is reversible with reoxidation

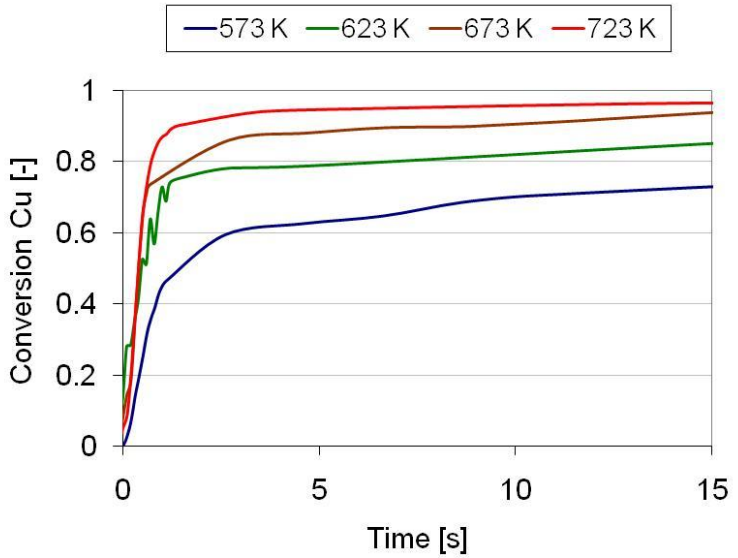
Results - In situ XAS measurements

- Catalyst red/ox cycles: LCF analysis

Conversion of CuO-phase of $CuO\text{-}CeO_2/Al_2O_3$ catalyst during reduction with $2\%C_3H_8/He$



Conversion of Cu-phase of $CuO\text{-}CeO_2/Al_2O_3$ catalyst during re-oxidation with $10\%\ O_2/He$



$$X_{CuO} = 1 - e^{-\frac{t}{\tau}}$$

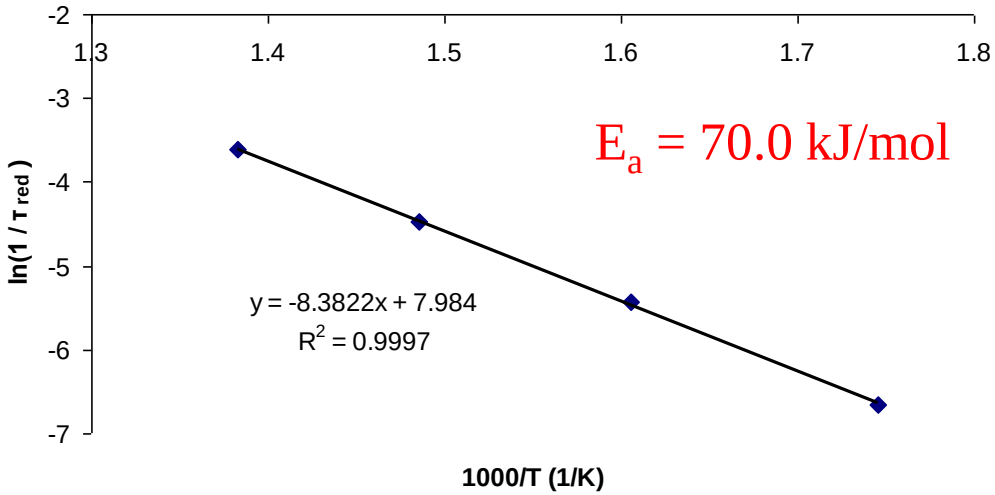
T (K)	573	623	673	723
τ_{red} (s)	782.7	229.6	88.3	37.2
τ_{ox} (s)	5.7	1.0	0.5	0.5

$$X_{Cu} = 1 - e^{-\frac{t}{\tau}}$$

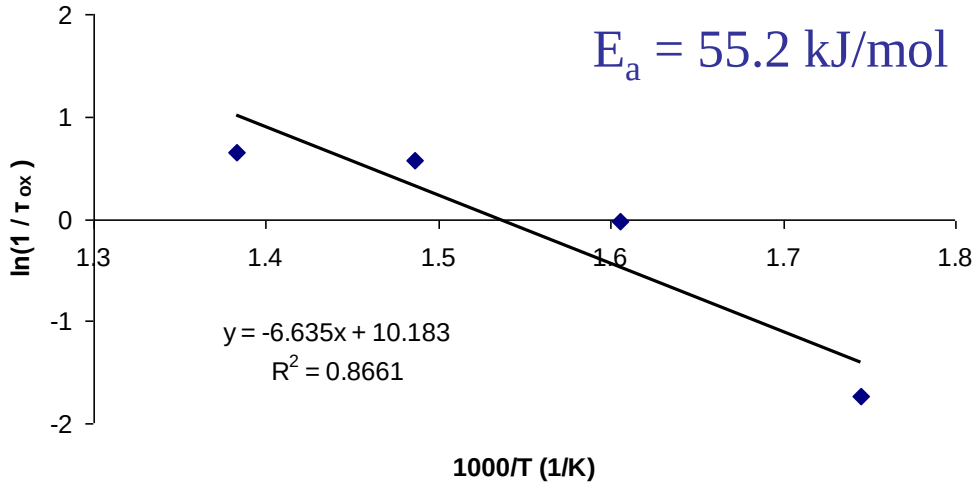
→ re-oxidation of catalyst occurs faster than its reduction at all T
→ both processes speed up with T

Results - In situ XAS measurements

- Catalyst red/ox cycles: LCF analysis
  - Activation energies for reduction & oxidation of $CuO\text{-}CeO_2/Al_2O_3$



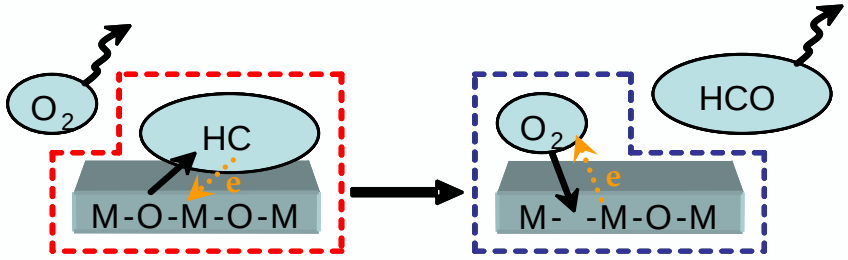
E_a = 70.0 kJ/mol



E_a = 55.2 kJ/mol

→ Catalyst reduction requires a higher E_a than catalyst oxidation

→ Therefore, during hydrocarbon oxidation over the metal oxide catalyst, a reaction that can occur via the following mechanism:



the first step (i.e. catalyst reduction) will be rate-determining

Results - In situ XAS measurements

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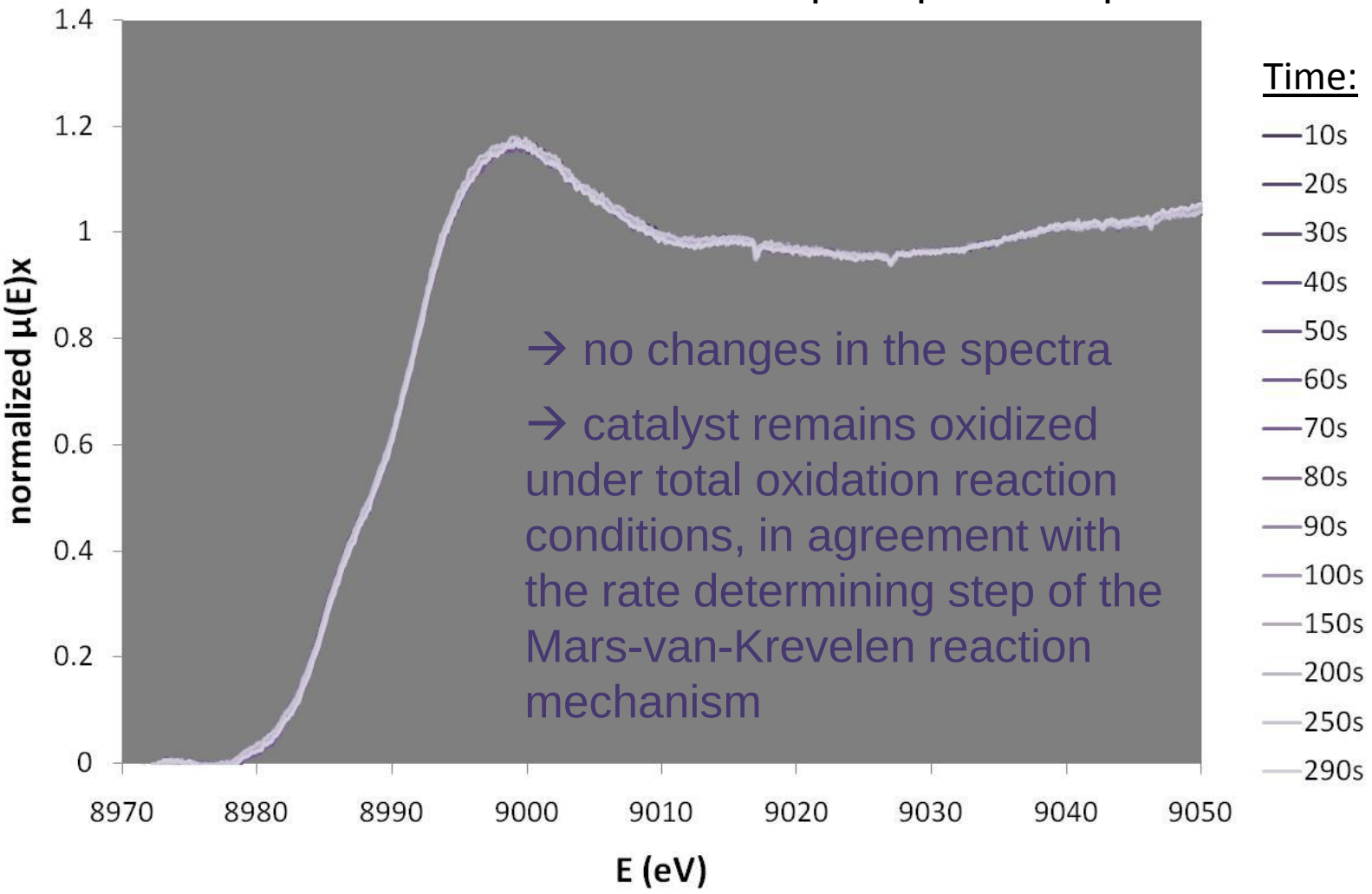
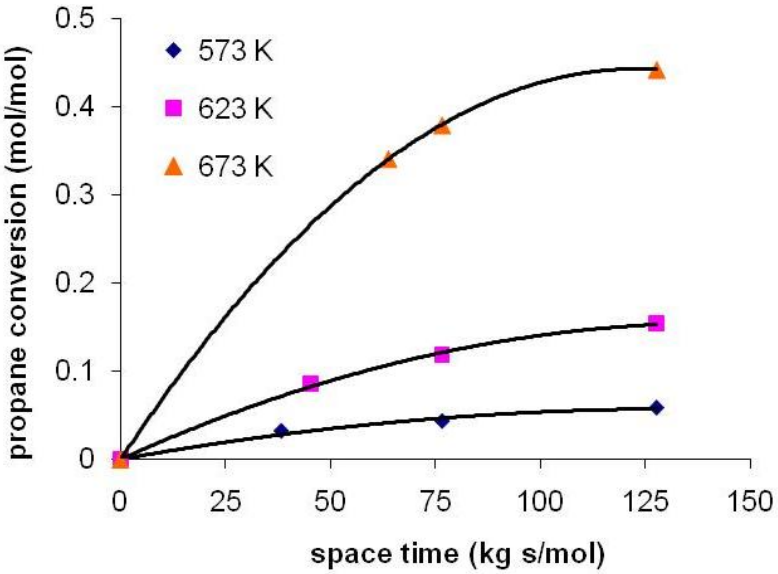


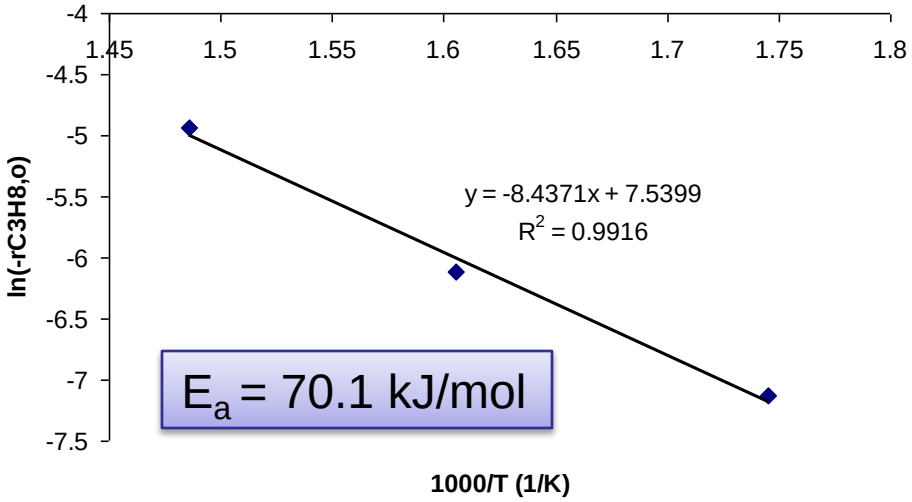
Results - In situ XAS measurements

- MS: Total oxidation reaction under steady state conditions



- $\gamma = y_{O2(0)} / y_{C3H8(0)} = 5$
- CO_2: main product
- CO: not observed
- C_3H_6: very small traces (ca. 100 ppm) within experimental error

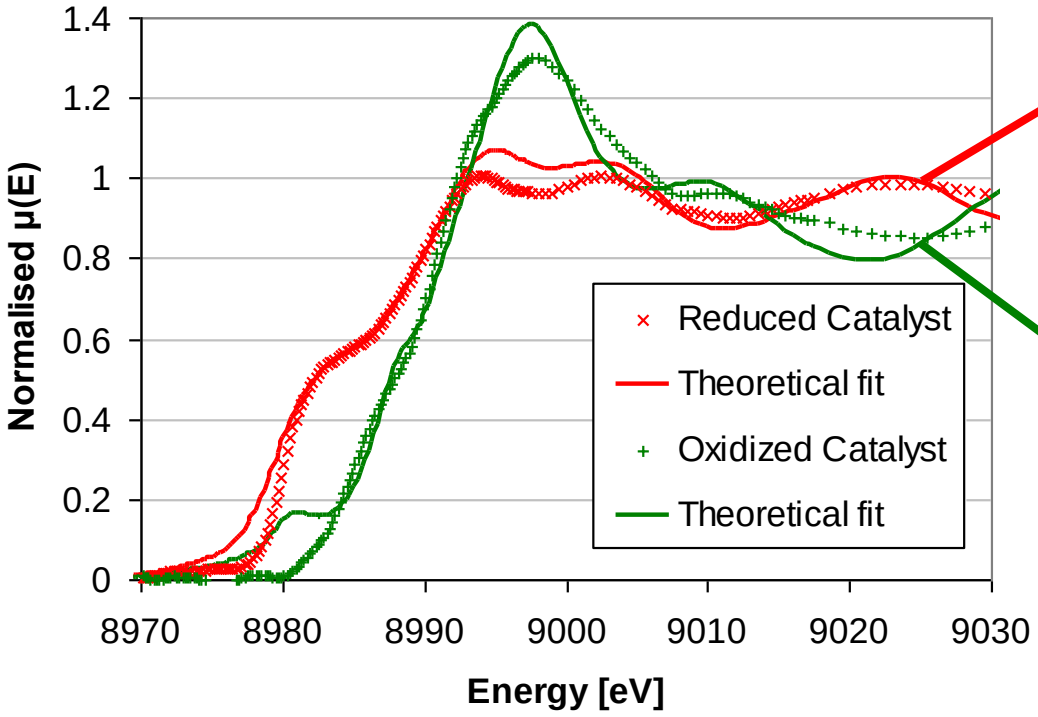
→ Apparent activation energy from MS analysis agrees with the apparent activation energy from the LCF analysis for catalyst reduction (rate-determining step)

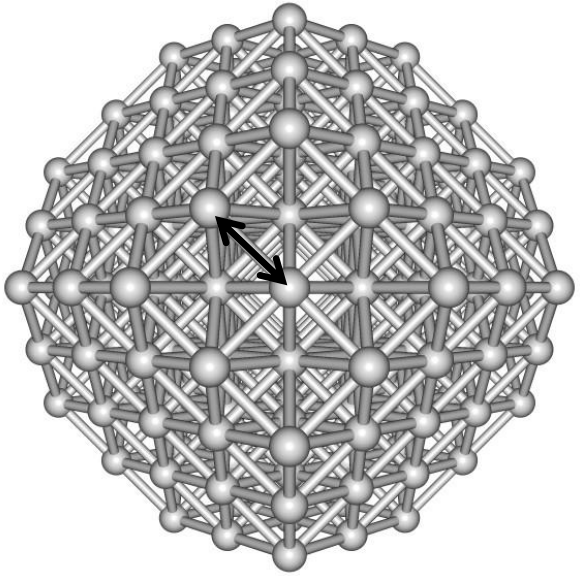


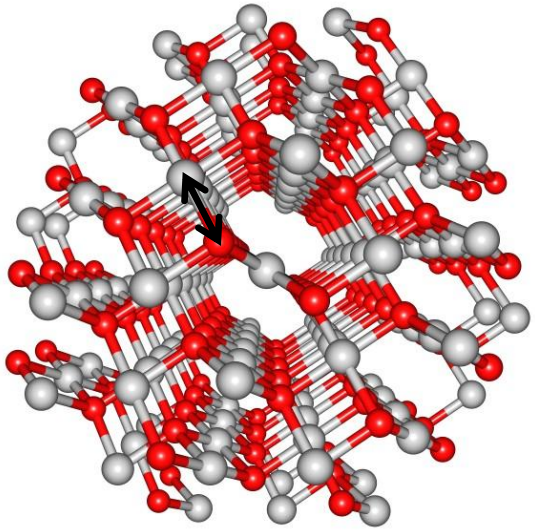
Results - Structure of the active phase

$CuO\text{-}CeO_2/Al_2O_3$ under steady-state reductive and oxidative conditions

Structure of active phase of catalyst modeled using the fcc Cu structure or the monoclinic CuO structure as input







→ Good agreement between theory and experiment (variance < 1%)

Results - Structure of the active phase

1. Reduced catalyst

Bond distance (Å)	Crystal structure	XANES fit values	
		Cu reference foil	Reduced catalyst
Cu-Cu	2.56	2.64	2.64

➢ Reduced catalyst same structure as metallic copper

2. Oxidized catalyst

Bond distance (Å)	Crystal structure	XANES fit values	
		CuO reference sample	Oxidized catalyst
Cu-O	1.95 - 1.96	2.01 - 2.02	2.10 - 2.11

➢ Oxidized catalyst CuO-like structure with larger Cu-O distances compared to reference

→ Weaker Cu-O bonds

Conclusions

- The copper phase of the catalyst remains oxidized during heating in He, pretreatment and total oxidation reaction conditions

- Based on the PCA and LCF results, three components are present during reduction and re-oxidation cycles (i.e. Cu(+2), Cu(+1) and Cu(0)) and a two-step mechanism is found

- Theoretical spectra have been successfully fitted to experimental XANES of the CuO-CeO_2/Al_2O_3 catalyst:

  ✓ No differences between the structure of the reduced catalyst and metallic copper

  ✓ The oxidized catalyst has a CuO-like structure with elongated Cu-O bonds, thus making removal of oxygen easier

Thank you for your attention

Questions ?